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# Use of Chemical Lasers to Determine the Rate Constants of Reactions Between Atoms and Molecules and the Rate Constants of the Relaxation of Vibrationally Excited Molecules

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The application of chemical lasers to the determination of the rate constants of reactions and of the relaxation of vibrational excitation is discussed. The following procedures are reviewed: the measurement of the time lag of the generation with respect to the leading edge of the pulse used to initiate the reaction, the measurement of the generation decay time, the use of competing reactions to measure the rate constants of "non-laser" reactions, and also methods of measuring the relative rate constants for the population of different levels in the reaction product (the "equal amplification temperature" method, the "zero amplification temperature" method, and the "grating selection" method). 71 references.

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## I. INTRODUCTION

Several methods of measuring the rate constants of reactions of atoms and radicals with molecules in the gas phase are available: spectroscopy, mass spectrometry, ESR, etc. However, the rate constants determined by different methods often show serious discrepancies, which complicate the selection of values for use in kinetic investigations. The differences in the rate constants of fast reactions of atoms and radicals with molecules are especially large. Furthermore, the range of application of these methods is often limited. Therefore the development of new experimental methods of measuring the rate constants of reactions of atoms and radicals with molecules is of great interest. A new method of measuring the rate constants of the relaxation of excited molecules would also be of great use.

The development of chemical lasers created the possibility of using the generation of radiation to measure the rate constants of the "pumping" reactions taking place in the lasers. These include, in particular, reactions such as

$$A + BC \rightarrow AB^{\dagger} + C$$

where A is an atom, BC is a molecule, and $AB^{\dagger}$ is a molecule formed in a vibrationally excited state. If the "pumping" reaction is a chain reaction the generation is determined by

several rate constants. For example,

$$Cl + H_2 \xrightarrow{k_1} HCl + H$$
$$H + Cl_2 \xrightarrow{k_2} HCl^{\dagger} + Cl .$$

The presence of several rate constants makes their determination more difficult. Furthermore, relaxation of the vibrationally excited molecules takes place in parallel with the other reactions, and this further complicates the determination of the kinetic constants $k_1$ and $k_2$. Nevertheless, as has been demonstrated experimentally, these difficulties can be overcome, and under certain conditions the kinetic constants of the reactions between atoms and molecules are relatively easily found from measurements of the oscillation parameters, with a precision at least equal to that of the more traditional methods.

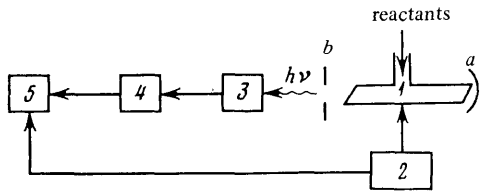



**Figure 1.** Block diagram of a chemical laser: *1*) laser tube, *2*) initiation system, *3*) monochromator, *4*) i.r. detector, *5*) oscillator.

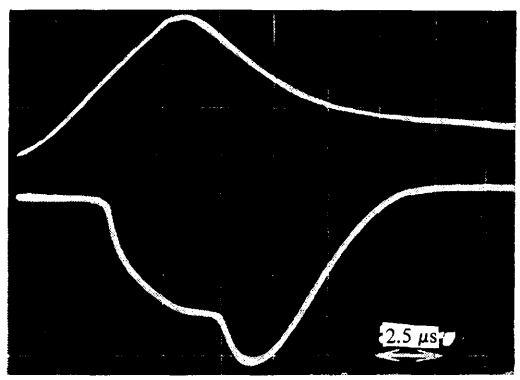



**Figure 2.** Oscillograms of the initiation pulse (upper trace) and the generation pulse (lower trace).

The basic principles of the determination of the kinetic and relaxation constants by using chemical lasers can be briefly illustrated as follows. The radiation from a chemical laser arises from a chemical reaction which produces excited molecules with a population inversion in different vibrationally excited states. A block diagram of the chemical laser is shown in Fig.1. The chemical reaction takes place in a cell containing the gas mixture within an optical resonator consisting of the mirrors *a* and *b* (the latter being half-silvered). The reaction in the chemical laser is initiated by atoms formed by the dissociation of molecules under the influence of a light pulse or a pulsed electrical discharge.

The length of the initiating pulse depends on the parameters of the initiating equipment used. The beginning of the initiation pulse is separated from the onset of laser generation by a time interval imposed by the need to reach the threshold concentration of the inverted population of excited molecules, which depends on the radiation losses in the resonator. The length of this time lag can be measured from oscillographic displays of the generation and initiation pulses, as shown in Fig.2.

## II. DETERMINATION OF THE CONSTANTS BY MEASURING THE OSCILLATION DELAY TIME

### 1. Principle of the Method

By measuring the oscillation delay time $t_1$ and equating the concentration of population-inverted molecules at time $t_1$ to the threshold value needed to satisfy the self-excitation condition we can obtain an equation for the required rate constant. Allowance must be made for the radiation losses in the resonator. The experimental conditions (initiation, pressure of reactants, amount of inert diluent) are chosen so as to make the consumption of reactants and the temperature rise of the working mixture during the time lag period negligibly small.

The possibility of measuring rate constants by the oscillation delay time method was first demonstrated by Basov and coworkers[1]. Chester and Hess[2] measured the dependence of the oscillation delay time (with respect to the leading edge of the initiating light pulse) on the rate constant of the "pumping" reaction, on the intensity of the initiating light flux, on the radiation losses in the resonator, on the composition and pressure of the gas mixture, and on the relaxation processes. They considered a chemical laser operating by the reaction RF + $H_2$ + B (where B is an inert gas). The atomic fluorine formed by the photolysis of RF takes part in the "pumping" reaction

$$F + H_2 \xrightarrow{k_{H_2}} HF^{\dagger} + H \qquad (1)$$

giving population-inverted $HF^{\dagger}$ molecules.

The basic kinetic equations are

$$d[RF]/dt = -s(t)[RF] \qquad (2)$$
$$d[F]/dt = qs(t)[RF] - k_{H_2}[F][H_2] \qquad (3)$$
$$d[H_2]/dt = -k_{H_2}[F][H_2] \qquad (4)$$
$$d[HF]/dt = -d[H_2]/dt \qquad (5)$$

where $s(t) = \Phi \int \sigma(\lambda) I(\lambda, t) d\lambda$, $\Phi$ is the yield of the photodissociation RF, $\sigma(\lambda)$ is the molecular absorption coefficient of RF, $I(\lambda, t)$ is the local intensity of the light flux at the wavelength $\lambda$, and $q$ is the number of F atoms formed by the dissociation of the RF molecule.

It was shown[2] that the temperature rise due to light absorption and to reaction (1) in time $t_1$ is negligible, and can be made even smaller by adding an inert gas to the reaction mixture. The frequency of the initiating light is chosen to lie outside the absorption bands of hydrogen and of the diluent gas. It was also shown[2] that the reactions of H, $H_2$, and HF with R and RF during time $t_1$ can be ignored, and so can also the recombination of atoms in the volume and at the walls. The process can be treated as quasi-isothermal.

In order to simplify the solution of the system of equations (2)–(5) the experimental conditions must be chosen so that the functions $I$ and $s$ can be expressed as

follows:

$$I(\lambda, t) = I_0(\lambda) t^m$$
$$s(t) = \Phi \int \sigma(\lambda) I_0(\lambda) d\lambda t^m = s_0 t^m, \; m > 0.$$

The initial conditions are $[F]_0 = [HF]_0 = 0$.

The system (2)–(5) can be transformed into

$$d[H_2]/dt = -k_{H_2}\left\{[H_2]_t - [H_2]_0 + q[RF]_0\left(1 - \exp\left(\frac{-s_0 t^{m+1}}{m+1}\right)\right)\right\}[H_2]_t \; , \quad (6)$$

By solving Eqn.(6) we can find $[HF]_t$:

$$[HF]_t = [H_2]_0 - [H_2]_t \; .$$

Let $\Delta n(t)$ be the difference in concentration between the $HF^\dagger$ molecules in the vibrationally excited levels $(v+1)$, $(J-1)$ and $v$, $J$, corresponding to the emission of a laser line with maximum amplification:

$$\Delta n(t) = [HF_{v+1, J-1}]_t - [HF_{v,J}]_t \; .$$

We then have $d[\Delta n(t)]/dt = f_{H_2} d[HF]/dt - k'[M]_t \Delta n(t)$, where $f_{H_2}$ is the difference between the probabilities of formation [by reaction (1)] of HF molecules in the upper $(v+1)$ and in the lower $(v)$ level, and $k'$ is the rate constant for the relaxation on M molecules.

Eqn.(6) can be integrated numerically, but alternatively the solution can simply be expanded in powers of $t$, retaining only the first-order terms. Since the time interval is small, deactivation occurs mainly by collisions with the initial $H_2$, RF, and diluent molecules, and we can assume that $[M]_t = [M]_0$. Therefore

$$\Delta n(t) \simeq \frac{f_{H_2} q k_{H_2} [RF]_0 [H_2]_0 s_0 t^{m+2}}{(m+1)(m+2)} \times \left\{1 - \frac{k_{H_2}[H_2]_0 t}{m+3} - \frac{k'[M]_0 t}{m+3} + \ldots\right\} \; , \quad (7)$$

Oscillation begins after time $t_1$ (measured from the beginning of the initiating pulse), when $\Delta n(t)$ reaches the critical (threshold) value $\Delta n_{thr}$, depending on the radiation losses in the resonator:

$$\Delta n(t_1) = \Delta n_{thr} \; , \quad (8)$$

Retaining only the lower-order term, i.e. ignoring the relaxation of the excited $HF^\dagger$ molecules, we obtain from (7) and (8) the following expression for the generation time lag, which includes the required constant $k_{H_2}$:

$$t_1 = \left\{\frac{(m+1)(m+2)\Delta n_{thr}}{f_{H_2} q k_{H_2} [RF]_0 [H_2]_0 s_0}\right\}^{1/(m+2)} . \quad (9)$$

If $m = 1$ we have

$$t_1 \sim (g_0/\alpha\alpha' s_0)^{1/3} p_{tot}^{-2/3}$$

where $p_{tot}$ is the total pressure of the mixture, $\alpha$ and $\alpha'$ are the mole fractions of $H_2$ and RF, and $g_0$ is the threshold amplification of the laser i.e. the amplification at the onset of oscillation.

The threshold amplification is related to the radiation losses in the resonator by the expression

$$(1-l)\exp(2g_0 L) = 1 \; , \quad (10)$$

where $l$ is the loss of radiation in the resonator for a single passage of the beam, determined by the precision of the optical assembly, the reflectivity of the mirrors, the transparency of the windows in the laser tube, etc. $L$ is the length of the optical path in the active medium.

Thus the rate constant of the "pumping" reaction can be determined, in principle, by measuring the oscillation delay time.

## 2. Rate Constants of the Reactions of Atoms and Radicals with Molecules

*a) Reaction of* F *atoms with* $CH_4$, HCl, *and* HBr. By using an $HF^\dagger$ laser the rate constants of the reactions of F atoms with other hydrogen-containing RH molecules can be determined from formula (9) if these reactions are used in "pumping" the laser. The equation for the "pumping" reaction (including the wanted $k_{RH}$ constant) is

$$F + RH \xrightarrow{k_{RH}} HF^\dagger + R \; , \quad (11)$$

Since formula (9) was obtained by ignoring the relaxation of the vibrationally excited $HF^\dagger$ molecules we must test whether the experimental conditions were correctly chosen, i.e. whether the condition $t_1 \propto p_{tot}^{-2/3}$ is obeyed when the intensity of the light flux is a linear function of time. If this expression applies we can find the ratio of the generation time lags in mixtures of $H_2$ + RF + B and RH + RF + B for equal partial pressure of RF and of the hydrogen donors. If $m = 1$ we have from Eqn.(9)

$$k_{RH} f_{RH}/k_{H_2} f_{H_2} = (t_1^{H_2}/t_1^{RH})^3$$

since the experimental conditions are specially chosen to make $\Delta n_{thr}$, $q$, $[RF]_0$, and $s_0$ the same in the two experiments, and $[H_2]_0 = [RH]_0$; $f_{RH}$ is a quantity analogous to $f_{H_2}$ and corresponds to reaction (11).

By using this method we have determined[3,4] the ratios $k_{CH_4}/k_{H_2} = 2 \pm 0.2$, $k_{HCl}/k_{H_2} = 0.25$, and $k_{HBr}/k_{H_2} = 1.3 \pm 0.2$. In the calculation we adopted the values $f_{CH_4} = 0.44$, $f_{H_2} = 0.37$, and $f_{HCl} = 0.33$ (obtained by averaging published data), and $f_{HBr} = 0.12$ (given by Jonathan and coworkers[5]).

*b) The* H + ClF *reaction.* The measurement of the oscillation delay time has been used to determine the rate constants of "pumping" reactions involving other atoms. Thus, the rate constant of the reaction H + ClF → $HCl^\dagger$ + F has been determined[6]. The experiment involved measuring the oscillation delay time on $HF^\dagger$ and $HCl^\dagger$ molecules in a chemical laser working on a mixture of ClF + $H_2$. The formation of F and Cl atoms took place by photodissociation of ClF.

The main sub-threshold processes are

$$ClF + h\nu \rightarrow Cl + F$$
$$F + H_2 \xrightarrow{k_{H_2}} HF^\dagger + H \quad (1)$$
$$H + ClF \xrightarrow{k_{ClF}^{(1)}} HCl^\dagger + F \quad (12)$$
$$H + ClF \xrightarrow{k_{ClF}^{(2)}} HF^\dagger + Cl \; , \quad (13)$$

The Cl + $H_2$ reaction is much slower than the F + $H_2$, and it can be ignored in a sub-threshold process. Theoretical calculations[7,8] suggest that $k_{ClF}^{(1)} < k_{H_2}$, $k_{ClF}^{(2)} < k_{H_2}$, and $k_{ClF}^{(1)} > k_{ClF}^{(2)}$: this suggestion was confirmed by kinetic measurements[9], which gave $k_{ClF}^{(1)}/k_{ClF}^{(2)} = 6.1$, and by i.r. chemiluminescence measurements[10], which gave $k_{ClF}^{(1)}/k_{ClF}^{(2)} = 6.7 \pm 0.8$. Therefore in the pre-threshold period we can legitimately ignore the formation of $HF^\dagger$ by reaction (13) in comparison to reaction (1), and assume that the consumption

of hydrogen atoms is negligible before the onset of generation on $HCl^{\dagger}$.

By solving the equation for the change in concentration of atomic fluorine with a linearly time-dependent light flux, and by integrating the equation for the change in concentration of HF, we can arrive at the threshold concentration of population-inverted excited $HF^{\dagger}$ molecules:

$$\Delta n_{\text{thr}}^{\text{HF}^{\dagger}} = f_{\text{H}_2} \int_0^{t_{l_1}} k_{\text{H}_2} [\text{H}_2]_0 [\text{F}]_t \, dt \qquad (14)$$

where $t_{l_1}$ is the generation time lag for the $P_2$ (3) transition of the HF molecules, which occurs first.

By the same procedure we can determine the threshold concentration of population-inverted excited $HCl^{\dagger}$ molecules:

$$\Delta n_{\text{thr}}^{\text{HCl}^{\dagger}} = f_{\text{ClF}} \int_0^{t_{l_2}} k_{\text{ClF}}^{(1)} [\text{ClF}]_0 [\text{H}]_t \, dt \qquad (15)$$

where $f_{\text{ClF}}$ is a coefficient analogous to $f_{\text{H}_2}$ corresponding to reaction (12), and $t_{l_2}$ is the oscillation delay time for the $P_2$ (5) transition of the HCl molecules. Furthermore

$$\Delta n_{\text{thr}}^{\text{HF}} / \Delta n_{\text{thr}}^{\text{HCl}} = \sigma_{v,J\to v',J'}^{\text{HCl}} / \sigma_{v',J\to v',J'}^{\text{HF}}$$

where $\sigma_{\nu,\ J \to \nu',\ J'}$ is the cross-section of the initiating radiation for the given vibrational–rotational transition of the HF and HCl molecules,

$$\sigma_{v,J\to v',J'} \simeq A_{v,J\to v',J'} M^{1/2} / \nu^3$$

where $A_{\nu,\ J \to \nu',\ J'}$ is the Einstein coefficient for the transition, $\nu$ is the transition frequency, and $M$ is the molecular weight.

From the ratio of Eqns.(14) and (15) we can obtain an expression for $k_{\text{ClF}}^{(1)}$. We calculated this constant by using Einstein coefficients taken from Refs.11 and 12, and an assumed $k_{\text{H}_2}$ value of $2.5 \times 10^{-11}$ cm$^3$ s$^{-1}$. The values $f_{\text{H}_2} = 0.36$ and $f_{\text{HCl}} = 0.31$, which describe the differences in occupancy probability of the $\nu = 2$ and $\nu = 1$ levels for HF and HCl molecules, were obtained by averaging published values for HF [13–15] and for HCl [16,17] (for the reaction $H + Cl_2 \to HCl^{\dagger} + Cl$). In this way the value $k_{\text{ClF}}^{(1)} = (3.7 \pm 0.4) \times 10^{-12}$ cm$^3$ s$^{-1}$ at 300 K was obtained for the first time. The i.r. chemiluminescence method[18] had yielded only the ratio of this constant to the rate constant of the reaction $H + Cl_2 \to HCl^{\dagger} + Cl$, equal to 1.99.

*c) The* $OD^{\dagger} + O_3$ *reaction.* Measurements of the oscillation delay time on $CO_2^{\dagger}$ molecules in a chemical laser working on an $O_3 + D_2 + CO_2$ mixture have been used[19] to determine the rate constant of the reaction between the OD radical and $O_3$. The main reactions in this mixture are

$$\begin{aligned}
&O_3 + h\nu \xrightarrow{k_0(t)} O(^1D) + O_2\\
&O(^1D) + D_2 \xrightarrow{k_1} OD^{\dagger}(v) + D\\
&D + O_3 \xrightarrow{k_2} OD^{\dagger}(v) + O_2\\
&OD^{\dagger}(v) + CO_2 \xrightarrow{k_3^v} OD^{\dagger}(v-1) + CO_2^{\dagger}\\
&O(^1D) + M \xrightarrow{k_4} O(^3P) + M\\
&OD^{\dagger}(v) + O_3 \xrightarrow{k_5} \begin{cases} \to DO_2 + O_2\\ \to OD + O + O_2\\ \to D + 2O_2 \end{cases}\\
&O(^1D) + O_3 \xrightarrow{k_6} O_2 + O_2\\
&OD^{\dagger}(v) + D_2 \xrightarrow{k_7^v} OD^{\dagger}(v-1) + D_2
\end{aligned}$$

where $CO_2^{\dagger}$ is a $CO_2$ molecule in the (00°1) state, $k_3^{\nu}$ and $k_7^{\nu}$ are the rate constants for the reactions in the OD radical in the level $\nu$, and $k_0(t)$ is the rate constant for the formation of $O(^1D)$ atoms from ozone under the influence of light.

### 3. Rate Constants of the Relaxation of Vibrational Excitation

The determination of the rate constants for the relaxation of vibrational excitation is very important in chemical kinetics, because vibrational excitation plays a key role in overcoming the activation barriers of reactions. The measurement of relaxation rate constants is especially important in the theory of chemical lasers because the intensity and duration of the generation are largely determined by relaxation processes.

The relaxation rate constants of vibrationally excited molecules can be measured, at present, by monitoring the intensity of laser-excited fluorescence at room temperature or by heating the gas mixture in a shock tube, or by the i.r. chemiluminescence method. As we shall show, the laser method (by measuring the generation time lag) can be used to determine the rate of relaxation and of transfer of vibrational excitation under appropriately chosen conditions (composition of the laser mixture, and other factors which determine the relaxation processes).

*a) The* $OD^{\dagger} + CO_2$, $OD^{\dagger} + D_2$ *processes.* Measurements of the oscillation delay time have shown[19] that at 300 K the rate constant of the deactivation of OD radicals ($\nu = 1$) by collisions with $D_2$ molecules is $k_7^1 = (3.1 \pm 0.7) \times 10^{-14}$ cm$^3$ s$^{-1}$, and the rate constant of the transfer of vibrational energy from the OD radical ($\nu = 1$) to $CO_2$ is $k_3^1 = (1.9 \pm 0.7) \times 10^{-12}$ cm$^3$ s$^{-1}$. The latter value is significantly higher than the value $k_3^1 = (0.5 \pm 0.25) \times 10^{-12}$ cm$^3$ s$^{-1}$ obtained[20] by a similar method but without allowance for the radiation loss in the resonator. Thus failure to correct for losses in the resonator can yield low values of the rate constant.

*b) The* $DF^{\dagger} + CO_2$ *reaction.* The measurement of the oscillation delay time has been used[1] to determine the rate constant of the transfer of vibrational energy from the $DF^{\dagger}$ molecule to the $CO_2$ molecule. The time lag of the generation was measured for the (00°1 → 10°0) transition of the $CO_2$ molecule in a chemical laser working with an $F_2 + D_2 + CO_2$ mixture. The most important elementary processes in such a mixture are

$$\begin{aligned}
&F_2 + h\nu \xrightarrow{k_0(t)} 2F\\
&F + D_2 \xrightarrow{k_1} DF(v) + D\\
&D + F_2 \xrightarrow{k_2} DF(v) + F\\
&DF(v) + CO_2 \xrightarrow{k_3} DF(v-1) + CO_2(00°1)\\
&CO_2(00°1) + M \xrightarrow{k_4} CO_2(00°0) + M \qquad (16)\\
&DF(v) + M \xrightarrow{k_5} DF + M \qquad (17)
\end{aligned}$$

where M is any molecule in the mixture.

In the initial stages of a chemical reaction, lasting ~$10^{-5}$ s after initiation, the processes (16) and (17) can be ignored, because the vibrationally excited states of the DF and $CO_2$ molecules have fairly long lifetimes. If we also ignore the time (~$10^{-6}$ s) for the establishment of a quasi-stationary concentration of D atoms according to the equation $k_1[F][D_2] = k_2[D][F_2]$ we may characterise the formation of vibrationally excited DF and $CO_2$ molecules by the expressions

$$(d/dt)[DF(v)] = W(t) - k_3[DF(v)][CO_2] \qquad (18)$$

$$(\mathrm{d}/\mathrm{d}t)[\mathrm{CO_2}(00°1)] = k_3[\mathrm{DF}(v)][\mathrm{CO_2}] \cdot \quad (19)$$

The reaction rate $W(t)$ in Eqn.(18) is given by

$$W(t) = 2k_1[\mathrm{F_2}][\mathrm{D_2}]\{1 + k_1[\mathrm{D_2}]/k_2[\mathrm{F_2}]\}^{-1}\int_0^t k_0(t')\,dt' \cdot \quad (20)$$

Integration of (18) and (19) gives

$$[\mathrm{CO_2}[00°1)]_t = k_1[\mathrm{CO_2}]\int_0^t\{\exp(-k_3[\mathrm{CO_2}]t')\int_0^{t'}\exp(k_3 \times \times[\mathrm{CO_2}]t'')W(t'')\,\mathrm{d}t''\}\,\mathrm{d}t' \cdot \quad (21)$$

Laser action begins at time $t_1$ after the front of the light pulse. During this time the occupancy of the upper lasing level of the $CO_2$ molecule reaches the threshold value. If this threshold value and the reaction rate $W(t)$ are known, the rate constant for the transfer of vibrational energy ($k_3$) can be determined by Eqn.(21).

It is assumed that the shape of the initiating pulse can be described by the expression

$$k_0(t) = \gamma_1 t\exp(-\gamma_2 t) \quad (22)$$

where the coefficients $\gamma_1$ and $\gamma_2$ define the amplitude and the duration of the pulse. From Eqns.(20)–(22) we obtain, after integration,

$$[\mathrm{CO_2}(00°1)](t_l) = W'f(\alpha, \gamma_2, t_l)$$

where $\alpha = k_3[\mathrm{CO_2}]$, and $W'$ is calculated by the expression

$$W' = 2k_1[\mathrm{F_2}][\mathrm{D_2}]\{1 + k_1[\mathrm{D_2}]/k_2[\mathrm{F_2}]\}^{-1}\gamma_1/\gamma_2^2 .$$

The quantity $W'$ is the reaction rate after the end of the initiation pulse, i.e. at $t \to \infty$: it can be obtained from the expression $P = \hbar\omega_L VW'$, where $P$ is the generated power, $\hbar\omega_L$ is the energy of the laser photon, and $V$ is the volume of the laser tube.

Ignoring the radiation loss in the resonator we can write

$$W'f(\alpha, \gamma_2, t_l) = [\mathrm{CO_2}]\exp(-\hbar\omega(10°0)/kT).$$

Inserting into this expression experimental values of $t_1$, $W'$, $\gamma_2$, and $[CO_2]$, and solving it for $\alpha$, we obtain the rate constant for the transfer of vibrational energy from DF to $CO_2$: $(1.5 \pm 0.5) \times 10^{-12}$ cm$^3$ s$^{-1}$ at 300 K. This is lower than the value obtained by other methods. For example, measurements of this constant from the laser-induced fluorescence of the DF molecules[21] and from their chemiluminescence[22] gave $6.4 \pm 10^{-12}$ and $5 \times 10^{-12}$ cm$^3$ s$^{-1}$ at 350 and 300 K respectively.

The rate constant for the transfer of vibrational excitation from DF to $CO_2$ has been determined[23] with allowance for the loss of radiation in the optical resonator. The expression for the threshold population density of the upper lasing level of $CO_2$ includes a term which corrects for these losses. Allowance was made also for the time to establish quasi-stationary concentrations of F and D atoms (through the formation of fluorine atoms in the working mixture under the influence of light from the pulsed lamp). The shape of the pulse of radiation emitted by the lamp was described by the expression $k_0(t) = \gamma_1 t^3\exp(-\gamma_2 t)$, which gives a more exact time dependence of the radiation intensity than the expression $k_0(t) = \gamma_1 t\exp(-\gamma_2 t)$. The rate of the chemical reaction at the end of the light pulse was determined by comparing the characteristics of the laser working under different conditions rather than by measuring the power of the laser emission. With these improvements the rate constant for the transfer of energy from the first vibrational level of the DF molecule to the $CO_2$ molecule was found to be $(8.2 \pm 0.5) \times 10^{-12}$ cm$^3$ s$^{-1}$, i.e. close to the values obtained by other methods.

*c) Relaxation of $HF^\dagger$ on chlorine fluorides.* The oscillation delay time method has been used to measure the rate constants of the relaxation of vibrationally excited $HF^\dagger$ molecules in order to determine the role of this relaxation on the reactions of other species used in the chemical lasers. From the laser generation in $ClF_n + H_2(CH_4)$ mixtures the rate constants of the relaxation of $HF^\dagger$ molecules on various chlorine fluorides have been determined[24]. The main pre-threshold processes in these lasers are

$$ClF_n + h\nu \xrightarrow{s(t)} ClF_{n-1} + F$$

$$F + RH \xrightarrow{k_{RH}} HF(v) + R$$

$$HF(v) + RH \xrightarrow{k_{rel}^{RH}} HF + RH$$

$$HF(v) + ClF_n \xrightarrow{k_{rel}^{ClF_n}} HF + ClF_n$$

where $k_{rel}^{RH}$ and $k_{rel}^{ClF_n}$ are the rate constants for the relaxation of HF(v) molecules on RH and $ClF_n$ molecules respectively. The relaxation of HF(v) on HF can be ignored under these conditions, since the concentration of HF has been shown[2] to be three orders of magnitude lower than the concentration of reactants during the period preceding the achievement of the oscillation threshold.

The spectral composition of the radiation shows that $v = 2$ for the $ClF_5 + H_2(CH_4)$ and $ClF + H_2(CH_4)$ systems, i.e. that the first transition is $P_2(3)$. For the $ClF_3 + H_2(CH_4)$ system, $v = 1$, and the first transition is $P_1(6)$. Hence in the latter system the following relaxation is fast:

$$HF(v=2) + ClF_3 \rightarrow HF(v=1) + ClF_3, \quad (23)$$

The kinetic equations for the concentration of atomic fluorine and for the density $\Delta n$ of population-inverted $HF^\dagger$ molecules take the form

$$\mathrm{d}[F]/\mathrm{d}t = s(t)[ClF_n]_0 - k_{RH}[F][RH]_0 \quad (24)$$

$$\mathrm{d}(\Delta n)/\mathrm{d}t = f_{RH}k_{RH}[F][RH]_0 - k\Delta n \quad (25)$$

where $s(t) = s_0 t\exp(-t/t_{max})$, $t_{max}$ is the time at which $s(t)$ reaches a maximum, and

$$k = k_{rel}^{RH}[RH]_0 + k_{rel}^{ClF_n}[ClF_n]_0.$$

In order to determine the relaxation rate constants we must choose conditions such that the pressure of chlorine fluoride is higher than that of RH, since the constants $k_{RH}$ and $k_{rel}^{RH}$ are quite large [according to Hancock and Green[25], $k_{rel}^{H_2} = 0.7 \times 10^{-12}$ cm$^3$ s$^{-1}$ for HF ($v = 1$)]. Solving the system of equations (24), (25) for the conditions

$$(k_{RH} + k_{rel}^{RH})[RH]_0 \ll k_{rel}^{ClF_n}[ClF_n]_0;\ 1/t_{max} \ll k_{rel}^{ClF_n}[ClF_n]_0$$

gives

$$\Delta n(t) = s_0\frac{f_{RH}k_{RH}}{2k^3}[(kt)^2 - 2kt + 2 - 2e^{-kt}], \quad (26)$$

The generation time lags with respect to the leading edge of the initiating pulse were measured for exit mirrors made of Ge and $CaF_2$ ($t_1'$ and $t_1''$ respectively). Since $g_0 \propto \Delta n$, by using the experimental time lags $t_1'$ and $t_1''$ for two different mirrors but identical compositions of the reactant mixture we can obtain from Eqn.(10)

$$g_0''/g_0' = \Delta n(t_1'')/\Delta n(t_1') = \lg(1 - l'')/\lg(1 - l') = C \quad (27)$$

where $l'$ and $l''$ characterise the radiative losses in the resonator with Ge and $CaF_2$ exit mirrors respectively. By combining (26) and (27) we obtain an equation for $k$. The constant $C$ can be calculated[2] from the condition $C = (t_1''/t_1')^3 \cong$

3 for low pressures. To study the relaxation on $ClF_3$ molecules the system of equations (24), (25) must be supplemented by an equation describing the population of the first level as a result of the relaxation of the second level during process (23).

**Table 1.** Relaxation rate constants ($10^{12}\ k_{rel}$, $cm^3\ s^{-1}$) of the vibrational excitation at 300 K, obtained by measurements of the time lag (I) and of the luminescence decay (II).

| Process | I | II |
|---|---|---|
| $OD(v=1)+CO_2 \rightarrow OD(v=0)+CO_2$ | 1.9±0.7 [19] | — |
| $OD(v=1)+D_2 \rightarrow OD(v=0)+D_2$ | 0.031±0.007 [19] | — |
| $DF(v=1)+CO_2 \rightarrow DF(v=0)+CO_2$ | 8.2±0.5 [23] | 6.4* [21]; 5 [22] |
| $HF(v=2)+ClF_5 \rightarrow HF(v=1)+ClF_5$ | 5.1±1.7 [24] | — |
| $HF(v=1)+ClF_5 \rightarrow HF(v=0)+ClF_5$ | | |
| $HF(v=2)+ClF \rightarrow HF(v=1)+ClF$ | 0.16±0.03 [24] | 0.02** [26] |
| $HF(v=1)+ClF \rightarrow HF(v=0)+ClF$ | | |
| $HF(v=1)+ClF_3 \rightarrow HF(v=0)+ClF_3$ | 5.6±1.7 [24] | 3.4 [27] |

*At 350 K.
**For the second process.

Numerical values of the relaxation rate constants are given in Table 1. The $k_{rel}$ values are combined constants for the relaxation of the second and first level for $ClF_5$ and ClF, and of the first level for $ClF_3$. These values agree in order of magnitude with the relaxation rate constants calculated from luminescence quenching data[26,27].

*d) The $HCl^\dagger$ + HCl relaxation.* Gorshkov and coworkers[28] measured the rate constant of the exchange reaction

$$HCl(v=m)+HCl(v=n) \rightarrow HCl(v=m-1)+HCl(v=n+1)$$

by comparing calculated and measured time dependences of the amplification in an HCl chemical laser. The apparatus consisted of two chemical lasers initiated by flash photolysis and working on an $H_2 + Cl_2$ mixture, mounted on a common optical axis, and operated in the oscillator regime and as an amplifier respectively. The reaction in the oscillator (with formation of a laser pulse) was started at a known time after the beginning of photolysis in the amplifier. The amplification of the oscillator output was determined in a series of experiments with increasing time intervals between the pulses in the amplifier and the oscillator. A computer programme based on the accepted model of the ($H_2 + Cl_2$) laser was used to calculate the time dependence of the population inversion and of the amplification for a single vibrational–rotational transition of the HCl molecule. A comparison of the experimental results with those of the computer model gave the probable range of values for the rate constant of the relaxation of $HCl^\dagger$ by $\nu$–$\nu$ exchange.

## III. DETERMINATION OF THE KINETIC CONSTANTS BY MEASURING THE OSCILLATION DECAY TIME

The measurement of the rate constant of the "pumping" reaction from the shape of the laser pulse depends on the fact that the relaxation of the lasing molecules, as well as several other processes, can be ignored under certain experimental conditions (low pressure, short and weak initiation reaction). In this case the decay of the laser signal is exponential, with an exponent depending only on time, on the rate constant of the "pumping" reaction, and on the initial concentration of the molecules taking part in that reaction.

### 1. Principle of the Method

The first reported measurement[29] of the rate constant of a "pumping" reaction from the shape of the laser pulse was aimed at determining the rate constants of the reactions of atomic fluorine with hydrogen, methane, and hydrogen chloride molecules. A more detailed description of the method appears in Ref.30, where an $NF_3 + H_2(D_2)$ laser is used to determine the rate constants of the reactions of atomic fluorine with hydrogen and deuterium molecules. The main processes in the working mixture of such a laser are:

$$NF_3 \xrightarrow{k_1} F + NF_2 \text{ (initiation)}$$

$$F + H_2 \xrightarrow{k^n_{H_2}} HF(v=n) + H \quad (1)$$

$$HF(v=n) + HF(v=m) \underset{k_3}{\overset{k_2}{\rightleftarrows}} HF(v=n-1) + HF(v=m+1) \quad (28)$$

$$HF(v=n) + H_2(v=m) \underset{k_5}{\overset{k_4}{\rightleftarrows}} HF(v=n-1) + H_2(v=m+1) \quad (29)$$

$$H_2(v=n) + H_2(v=m) \underset{k_7}{\overset{k_6}{\rightleftarrows}} H_2(v=n-1) + H_2(v=m+1) \quad (30)$$

$$HF(v=n) + M \xrightarrow{k_8} HF(v=n-1) + M \quad (31)$$

$$H_2(v=n) + M \xrightarrow{k_9} H_2(v=n-1) + M \quad (32)$$

$$HF(v=n) \xrightarrow{k_7} HF(v=n-1) + h\nu_{n,n-1} \quad (33)$$

$$HF(v=n) + h\nu_{n,n-1} \underset{}{\overset{}{\rightleftarrows}} HF(v=n-1) + 2h\nu_{n,n-1} \text{ (stimulated emission)}.$$

In this scheme (1) is the "pumping" reaction, (28), (29), and (30) describe vibrational–vibrational energy exchange (for seven HF levels and three $H_2$ levels), (31) and (32) are vibrational–translational energy exchange processes, and (33) is the spontaneous emission from $HF^\dagger$.

Difficulties in this method arise from the influence of a large number of elementary processes on the rate of excitation of the vibrational levels of the HF molecules, which determines the power of the oscillation. If the rates of these processes are comparable, it is not easy to extract information on any particular elementary act from the time dependence of the laser power. Therefore the constants can be determined by the "oscillation decay" method only if the parameters of the system are chosen so that the elementary act of interest plays a predominant role among all the other possible elementary acts.

Numerical calculations[30] for the $NF_3 + H_2$ system have shown that such a regime can be realised at low pressures of the $NF_3 + H_2$ mixture ($\leq$10 mmHg) and by using a weak initiation of the reaction ($[F]_0 \leq 10^{14}\ cm^{-3}$). The calculations took account of reactions (1) and (28)–(33). They led to the conclusion that under certain conditions the main contribution to the excitation of the vibrational levels of HF comes from the reaction $F + H_2 \rightarrow HF(\nu = n) + H$. The contributions from other processes are at least two orders of magnitude lower (Fig.3).

By examining the material balance equations for the density of photons in the resonator and for the occupancy of the vibrational levels of HF we can show that in the quasi-stationary approximation the power of the laser radiation (in the absence of relaxation processes) is proportional to the rate of "pumping" by the reaction $F + H_2 \rightarrow HF^\dagger + H$. The balance equations which allow for the chemical pumping and

for the stimulated emission are

$$dn_v/dt = \alpha_v W(t) - B_{v,v-1}\Delta_{v,v-1}\rho_{v,v-1} + B_{v+1,v}\Delta_{v+1,v}\rho_{v+1,v}$$

$$d\rho_{v,v-1}/dt = B_{v,v-1}\Delta_{v,v-1}\rho_{v,v-1} - \rho_{v,v-1}/\tau_p$$

where $n_\nu$ is the population density of the vibrational level $\nu$, $\rho_{\nu,\nu-1}$ is the density of photons in the resonator, $\alpha_\nu$ is the probability of forming a molecule in the level $\nu$ by an elementary reaction act, $B_{\nu,\nu-1}$ is the Einstein coefficient for the stimulated emission by the transition $\nu \to \nu - 1$, $\tau_p$ is the lifetime of a photon in the resonator, $\Delta_{\nu,\nu-1}$ is the difference in population density between the levels $\nu$ and $\nu - 1$, and $W(t)$ is the reaction rate, i.e.

$$W(t) = k_{H_2}[F][H_2], \qquad (34)$$

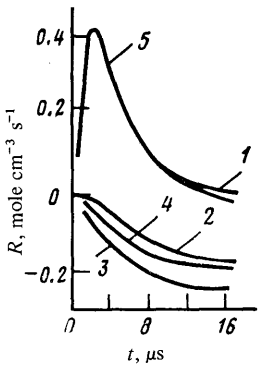



**Figure 3.** Rate of excitation $R_i$ of the HF vibrational levels in the $i$-th process as a function of time $t$: *1*) $10^5 R_1$, *2*) $10^8 R_{28}$, *3*) $10^7 R_{29}$, *4*) $10^8 R_{31}$, *5*) $10^5$ d[HF($\nu = 2$)]/d$t$.

The suggestion that laser action takes place in one vibrational–rotational transition of each band ($\nu \to \nu - 1$) does not materially affect these conclusions[30].

The power density of the radiation emerging from the resonator is

$$P = \sum_v \frac{\rho_{v,v-1}}{\tau_p}\hbar\omega_{v,v-1}.$$

For the scheme involving four equidistant levels in the quasi-stationary approximation ($d\rho_{\nu,\nu-1}/dt = d\Delta_{\nu,\nu-1}/dt = 0$) we can write

$$P = \frac{1}{2}\hbar\omega_L W(t)(3\alpha_3 + \alpha_2 - \alpha_1 - 3\alpha_0) \qquad (35)$$

where $\hbar\omega_L$ is the energy of the laser photon.

Since the concentration of fluorine atoms $[F]_0$ created by the initiating pulse is small in comparison with the initial concentration of hydrogen molecules $[H_2]_0$ we can put $[H_2]_t = [H_2]_0$. Then,

$$[F]_t = [F]_0 \exp(-k_{H_2}[H_2]_0 t), \qquad (36)$$

In the derivation of Eqn.(36) the initiating pulse was assumed to be shorter than the characteristic time of the chemical reaction. This assumption is valid under the chosen experimental conditions. From (34) and (36) we arrive at

$$\ln P(t) \sim k_{H_2}[H_2]_0 t.$$

Thus, having determined $\tau$ (the time constant of the decay of the laser pulse), and knowing $[H_2]_0$, we can calculate the rate constant:

$$k_{H_2} = 1/\tau[H_2]_0.$$

The heating of the gas by elastic collisions of electrons and heavy particles can be shown to be negligible[31]. The heating effect of the chemical reaction on the gas mixture is estimated to be less than 1 K. Heating through the relaxation of the vibrational energy of the molecules excited by the discharge becomes appreciable (at low pressures) during the later stages of the process, when the chemical reaction has gone to completion. We can therefore assume that the reaction takes place isothermally at the wall temperature of the reaction vessel.

The $k_{H_2}$ and $k_{D_2}$ constants have been measured[30] at 195 and 295 K. The $k_{H_2}$ value for 295 K was close to the recommended[32] value $k_{H_2} = 2.5 \times 10^{-11}$ cm$^3$ s$^{-1}$. On the other hand the value $k_{H_2} = 6.3 \times 10^{-11}$ cm$^3$ s$^{-1}$, given in Ref.29 for room temperature, is too high, possibly because some of the fluorine atoms taking part in the reaction F + $H_2$ had an excess of energy, acquired during the photo-initiation. Under the chosen experimental conditions[29] the thermalisation time of the "hot" fluorine atoms could have been comparable to the time of the chemical reaction.

The decay of laser action for reactions initiated by an electric discharge has been used to determine the rate constants of reactions between fluorine atoms and a series of organic and of inorganic molecules[33]. However, the experimental conditions were not optimised for the measurement of rate constants, and the results may be in error by a factor of 1.5–3.

### 2. Comparison of the Rate Constants of the Reactions of Fluorine Atoms Determined by Different Methods

Rate constants determined from measurements of the delay of time agree satisfactorily with those calculated from the decay of laser oscillation[3]. Measurements of the oscillation decay time in conjunction with initiation by an electric discharge have been used to determine the rate constants of the reactions of fluorine atoms with hydrogen, methane, and hydrogen chloride molecules. By measuring the generation time lag (with photo-initiation) the ratios $k_{CH_4}/k_{H_2}$ and $k_{HCl}/k_{H_2}$ have been determined. The results are summarised in Table 2, from which we note that in spite of the different methods of initiation the agreement between the various results is generally good.

For comparison Table 2 also gives the rate constants obtained by other methods. For the $k_{H_2}$, $k_{CH_4}$, and $k_{HCl}$ constants, which have been measured in many laboratories, we have adopted the values recommended in recent review articles[32,34]. It is evident from Table 2 that the rate constants determined by laser methods are fully consistent with those obtained by other methods.

Thus, in spite of the many assumptions necessarily made in the laser methods of determining kinetic constants (neglect of the relaxation of the population-inverted molecules, constancy of reactant concentrations, and failure to allow for the slower reactions), the reaction rate constants measured by these methods are as precise as those measured by other methods.

## IV. THE COMPETING REACTION METHOD OF MEASURING THE RATE CONSTANTS OF REACTIONS IN CHEMICAL LASERS

The main weakness of the above laser methods of determining the kinetic constants of reactions between atoms and molecules is their severely limited range of application (to "pumping" reactions only). The scope of the method was broadened very substantially by our development[43] of a variant based on the standard kinetic method of using competing reactions. A substance whose molecules can interact with the atoms involved in the "pumping" reaction is introduced into the active medium of the laser. As a result, the atoms are contributing to two reactions in parallel within the chemical laser: 1) the "pumping" reaction, leading to laser action, and 2) the competing reaction, which suppresses the rate of the "pumping" reaction by lowering the concentration of the participating atoms. This leads to an increase in the oscillation delay time, and to a decrease in the decay time constant of the laser action. By measuring these characteristic times in the presence and in the absence of the competing reaction we can determine its rate constant.

**Table 2.** Comparison of the rate constants for F + X reactions determined by different methods at 300 K.

| X | $10^{11}k_X$, $cm^3 s^{-1}$ | $k_X/k_{H_2}$ | Method |
|---|---|---|---|
| $H_2$ | 2.5 | — | I [32] |
| $H_2$ | 2.4±0.1 | — | II [30] |
| $H_2$ | 2.2±0.4 | — | II [3] |
| $D_2$ | 2.12±0.10 | 0.86 | II [30] |
| $D_2$ | — | 0.56 | III [15] |
| $D_2$ | — | 0.62 | IV [35] |
| $D_2$ | — | 0.61 | V [36] |
| $D_2$ | — | 0.52 | VI [37] |
| $D_2$ | 2.14 | 0.59 | VII [38] |
| $CH_4$ | 8 | — | I [32] |
| $CH_4$ | 7.2±1.2 | — | I [34] |
| $CH_4$ | 4.6±0.7 | 2.1 | II [3] |
| $CH_4$ | — | 2±0.2 | VIII [3] |
| HCl | 1.3±0.3 | — | I [34] |
| HCl | 0.7±0.2 | 0.3 | II [3] |
| HCl | — | 0.25 | VIII [3] |
| HBr | — | 0.65* | VIII** [4] |
| HBr | — | 0.87±0.14* | IX [5] |
| HBr | — | 0.68* | IX [39] |
| $Cl_2$ | 12.5±1.2 | — | VIII [3] |
| $Cl_2$ | 11±3 | — | VI [40] |
| $Cl_2$ | 16±5 | — | VI [41] |
| $Br_2$ | 16±3 | — | VIII [4] |
| $Br_2$ | 31±9 | — | VI [41] |

Notes. The $k_X$ values for X = $O_2$ + $O_2$ and X = $O_2$ + $N_2$, determined by measuring the time lag[4] and by ESR respectively[42], are (1.0 ± 0.3) × $10^{-32}$ and (1.4 ± 0.4) × $10^{-32}$ $cm^6$ $s^{-1}$. Methods: I) recommended value, II) measurement of decay time, III) chemical laser, IV) competing reactions, V) calculated, VI) mass spectrometric, VII) ESR, VIII) measurement of delay time, IX) i.r. chemiluminescence.

*Value of $k_{HBr}/k_{CH_4}$.

**Assuming $k_{CH_4}/k_{H_2}$ = 2 (after Ref.3).

The application of the competing reaction method in chemical lasers has substantially increased the range of reactions whose rate constants can be measured by laser methods. By using competing reactions we can measure the rate constants of a large number of reactions which do not give rise to laser emission. The combined method has been applied in a number of reactions between fluorine atoms and various molecules.

### 1. Application of the Method in Measurements of the Oscillation Delay Time

The competing reaction method was first used in conjunction with measurements of the delay time to determine the rate constant of the F + $Cl_2$ reaction[3], by measuring the generation time lag in $H_2$ + RF + He and $H_2$ + RF + $Cl_2$ + He mixtures.

The main processes in the $H_2$ + RF + $Cl_2$ + He mixture are

$$RF + h\nu \rightarrow R + F$$

$$F + H_2 \xrightarrow{k_{H_2}} HF^{\dagger} + H \qquad (1)$$

$$F + Cl_2 \xrightarrow{k_{Cl_2}} ClF + Cl\,. \qquad (37)$$

The Cl + $H_2$ reaction can be ignored, because its rate is much lower than the rates of reactions (1) and (37).

By solving the equation for the time dependence of the concentration of atomic fluorine (assuming a linear time dependence of the initiating light flux and constant reactant concentrations) we can find the threshold concentration of population-inverted excited $HF^{\dagger}$ molecules:

$$\Delta n_{thr} = f_{H_2} \int_0^{t_3} k_{H_2} [H_2]_0 [F]_t \, dt\,.$$

The delay times of laser action by the $P_2(3)$ transition of the $HF^{\dagger}$ molecule were measured in $H_2$ + RF + $Cl_2$ + He and $H_2$ + RF + He mixtures ($t_{l_1}$ and $t_{l_2}$ respectively). Under these conditions $\Delta n_{thr\,1} = \Delta n_{thr\,2}$. Hence we can obtain a transcendental equation for determining $k_{Cl_2}$.

The same method was used[4] to determine the rate constants of the reactions

$$F + Br_2 \xrightarrow{k_{Br_2}} FBr + Br$$

$$F + O_2 + O_2 \xrightarrow{k_{O_2}} FO_2 + O_2\,,$$

### 2. Application of the Method in Measurements of the Oscillation Decay Time

*a) Principle of the method.* The oscillation decay time is measured for the $HF^{\dagger}$ molecules of a chemical laser operating on a mixture of RF + $H_2$ + X + He, where X is a molecule for which we wish to determine the time constant of the reaction with atomic fluorine ($k_X$).[43] In this laser reaction (1) is the "pumping" reaction. In the presence of the X molecules, which react with fluorine atoms, reaction (1) competes with the following reaction:

$$F + X \xrightarrow{k_X} \text{products}\,. \qquad (38)$$

Reaction (38) lowers the rate of reaction (1) and shortens the time constant of the decay of the laser action. Since at low pressures and for short and weak initiating pulses the oscillation strength is proportional[30] to the rate of reaction (1), and therefore to the concentration of atomic fluorine, the decay of the signal in this case is described by an exponential function with the exponent

$$-(k_{H_2}[H_2]_0 + k_X[X]_0)t$$

where $[H_2]_0$ and $[X]_0$ are the initial concentrations of hydrogen molecules and of the additive respectively. By

measuring the time constant of the decay of the laser signal ($\tau$), and knowing $[H_2]_0$ and $[X]_0$, we can calculate $k_X$:

$$k_X = 1/\tau[X]_0 - k_{H_2}[H_2]_0/[X]_0.$$

The rate constant of the reference reaction ($k_{H_2}$) is accurately known. If necessary, other chemical laser "pumping" reactions can be used as the reference reaction.

This method was first used[3] to determine the rate constant of the reaction $F + Cl_2 \xrightarrow{k_{Cl_2}} FCl + Cl$, in conjunction with the following "pumping" reactions:

$$F + CH_4 \rightarrow CH_3 + HF^\dagger$$
$$F + HCl \rightarrow HF^\dagger + Cl.$$

The constant $k_{Cl_2} = (6.2 \pm 3.1) \times 10^{-11}$ cm$^3$ s$^{-1}$ at 300 K was obtained.

*b) Use of the method to measure the rate constants of the reactions of fluorine atoms with organic molecules containing multiple bonds.* The determination of these constants is complicated by the simultaneous presence of two reactions: the removal of an F atom with formation of HF and the addition of an F atom at the multiple bond. The addition reaction does not lead to the formation of $HF^\dagger$ molecules with a population inversion. The removal reaction may cause inversion [for example, $F + C_2H_4$, $F + C_3H_6$, $F + iso\text{-}C_4H_8$, $F + (CH_3)_2CO$], or it may produce HF molecules without population inversion (for example, in the $F + C_6H_6$ and $F + CH_3CN$ reactions).

**Table 3.** Rate constants of F + M reactions (where M is a molecule containing multiple bonds) at 300 K.

| M | $10^{10}\,k_{tot}$, cm$^3$ s$^{-1}$ | $k_{rem}/k_{add}$ | $10^{10}\,k_{rem}$, cm$^3$ s$^{-1}$ | $10^{10}\,k_{add}$, cm$^3$ s$^{-1}$ | Method*** |
|---|---|---|---|---|---|
| $C_2H_4$ | 1.4±0.4 [43] | 0.43 [46] | 0.4* [45] | 1.0* [45] | I |
| $C_2H_4$ | — | — | 0.4 [39] | 1.5** [49,50] | — |
| $C_3H_6$ | 1.9±0.4 [45] | 1.0 [47] | 1.0* [45] | 1.0* [45] | II |
| iso-$C_4H_8$ | 2.7±0.5 [45] | 1.2 [47] | 1.5* [45] | 1.2* [45] | II |
| $(CH_3)_2CO$ | 3.2±0.8 [44] | — | 1.3 [39] | 1.9 [44] | I |
| $CH_3CN$ | 0.52±0.13 [44] | — | 0.15 [39] | 0.37 [44] | I |
| $C_6H_6$ | 1.3±0.4 [43] | — | 0.8 [39] | 0.5 [43] | I |
| $C_6H_6$ | 2.7±0.9** [48] | — | — | — | III |

*Calculated by using the $k_{rem}/k_{add}$ ratio given in Refs. 46 and 47.

**At 283 K.

***The following methods were used to determine the total interaction constant $k_{tot}$: I) measurement of the oscillation decay time in conjunction with a competing reaction, II) measurement of the oscillation decay time, III) radio-gas chromatography.

However, even if laser action takes place with the HF molecules, it can be so weak as to make the rate constant of the reaction impossible to measure otherwise than by the competing reaction method. This situation exists, for example, in the reactions $F + C_2H_4$ and $F + (CH_3)_2CO$, and therefore the rate constants of these reactions were determined by the present method by arranging for these reactions to compete with the pumping reaction $F + H_2$. The same method was used to determine the rate constants of the reactions $F + C_6H_6$ and $F + CH_3CN$, since in these systems oscillation does not take place on HF. The rate constants of the reactions $F + C_3H_6$ and $F + iso\text{-}C_4H_8$ were measured in the usual way by using the formula $k_{RH} = 1/\tau[RH]_0$, where $RH = C_3H_6$ or $iso\text{-}C_4H_8$, since in these systems adequate laser action on the HF molecules was obtained[45]. The measured rate constants are listed in Table 3.

The main disadvantage of applying this method of measuring rate constants to molecules with multiple bonds is that the relative contributions of the addition and removal reactions cannot be distinguished, since the measurement gives the sum of the rate constants of these reactions. However, by using existing data on the ratios of these constants[46,47] and on the rate constants of the removal reactions calculated from i.r. chemiluminescence measurements[39] we can arrive at the separate rate constants of the removal reaction ($k_{rem}$) and of the addition reaction ($k_{add}$) for these molecules (Table 3). It is clear from Table 3 that the agreement between constants determined by the laser method[45], the luminescence method[39], and the radio-gas chromatography method[48–50] is satisfactory.

Of course, if the method is applied to molecules in which the addition reaction cannot take place these complications disappear, and the constants can be determined directly. The method is suitable also for other classes of molecules. The laser method in the competing reaction variant can be applied to any atom able to undergo a reaction in which excited molecules showing a population inversion are formed.

## V. METHODS OF MEASURING THE RELATIVE RATE CONSTANTS FOR THE POPULATION OF DIFFERENT LEVELS IN THE REACTION PRODUCT

Measurements of the occupancy of different vibrational levels in the molecules of reaction products can be relevant in various applications of chemical kinetics. The use of chemical lasers can offer quantitative information on the population $N_v$ of the vibrational levels of reaction products and on the relative rate constants $k_v$ for the formation of the product in different vibrational states.

### 1. The "Equal Amplification Temperature" Method

The "equal amplification temperature" method allows the ratio of the rate constants $k_v/k_{v-1}$ for the $v \rightarrow v-1$ transition, which has the maximum amplification, to be measured directly. The method was first proposed[51] for the $F + H_2$ and $F + CH_4$ reactions. By careful temperature control in chemical lasers operating with $UF_6 + H_2(D_2)$ and $UF_6 + CH_4(CD_4)$ mixtures, and using photo-initiation, conditions giving two vibrational–rotational transitions simultaneously and with the same amplification were obtained. The ratio $N_v/N_{v-1}$ of the occupancies of the states taking part in the first transition at the generation threshold was determined. This ratio can be identified with the ratio $k_v/k_{v-1}$ if vibrational deactivation can be ignored. Addition of a known amount of inert diluent is sufficient to bring about a rapid rotational equilibrium[52]. Under these conditions the rotational temperature of the system is close to the initial temperature of the laser mixture, which is determined by the external application of heat to the laser tube. The self-heating of the mixture as a result of the laser reaction is negligible.

The time lag between the beginning of the $P_2(4)$ and of the $P_2(3)$ transition of the HF molecule in the $UF_6 + H_2$ system was found to decrease as the temperature of the laser tube was increased, the intensity of the $P_2(3)$ transition

decreasing while that of the $P_2(4)$ transition increased. The temperature corresponding to equal time lags (and amplifications) for the $P_2(3)$ and $P_2(4)$ transitions was found. This temperature was termed the "equal amplification temperature" for the $P_2(3)$ and $P_2(4)$ transitions.

According to Patel[53], the relative amplification $\alpha_v(J)$ of the transition ($v \to v-1$, $J-1 \to J$) is

$$\alpha_v(J) = \text{const}\ \frac{JN_{v-1}}{kT_n^{1/2}T_{\text{rot}}}\left[\frac{N_v}{N_{v-1}}B_v \exp\left(\frac{-B_vJ(J-1)}{kT_{\text{rot}}}\right) - B_{v-1}\exp\left(\frac{-B_{v-1}J(J+1)}{kT_{\text{rot}}}\right)\right] \quad (39)$$

where $k$ is Boltzmann's constant, $B_v$ is the rotational constant of the vibrational level $v$, $T_n$ is the translational temperature, and $T_{\text{rot}}$ is the rotational temperature (with $T_n = T_{\text{rot}}$ in the present case). When the two transitions $P_v(J)$ and $P_v(J+1)$ have equal amplifications, i.e. $\alpha_v(J) = \alpha_v(J+1)$, the ratio $N_v/N_{v-1}$ can be obtained from the previous equation:

$$\frac{N_v}{N_{v-1}} = \frac{B_{v-1}}{B_v} \times \times \frac{J\exp[-B_{v-1}J(J+1)/(kT_{\text{rot}})] - (J+1)\exp[-B_{v-1}(J+1)(J+2)/(kT_{\text{rot}})]}{J\exp[-B_vJ(J-1)/(kT_{\text{rot}})] - (J+1)\exp[-B_vJ(J+1)/(kT_{\text{rot}})]} \quad (40)$$

where $T_{\text{rot}}$ is the equal amplification temperature. As was stated above, $N_v/N_{v-1} = k_v/k_{v-1}$.

The method has been used to obtain the ratios $k_2/k_1$ for the reaction F + $H_2$,[51] $k_3/k_2$ for the reaction F + $D_2$,[51] $k_3/k_2$ for the reaction F + $CCl_3D$,[54] and $k_4/k_3$ for the reaction F + HI.[55]

Berry and Pimentel[56] have modified Eqn.(40) in order to allow for vibrational–rotational interaction, which had been previously ignored. They also examined the effect of pressure on the shape (width) of the line and on the amplification, and they extrapolated their experimental results to low pressures. At the equal amplification temperature they measured the following ratios of the rate constants for the population of the levels in the HCl molecules produced by the light-induced removal of HCl from dichloroethylene: $k_3/k_2$ for the 1,1 isomer and $k_2/k_1$ for the *cis*- and *trans*-1,2 isomers.

The "equal amplification temperature" method gives only the $k_v/k_{v-1}$ ratio: for the other ratios it can only give upper limits, since when the oscillation threshold is reached these transitions are affected by the previous laser emission. The method has been improved[57] by using a "tandem" chemical laser with two laser tubes in the same resonator simultaneously initiated by flash photolysis. In this case the ratio of the rate constants could be measured even for transitions which do not give maximum amplification. For the photodehydrochlorination of dichloro-ethylene the $k_3/k_2$ and $k_2/k_1$ ratios of the HCl molecules were obtained for the 1,1 isomer and for the *cis*-1,2 isomer.

Molina and Pimentel[58] have described another improvement of the "equal amplification temperature" method, involving the inclusion of a diffraction grating in the optical resonator. This allows previous selection of the vibrational–rotational transitions, and hence it allows the measurement of different $k_v/k_{v-1}$ ratios (not only those corresponding to transitions with maximum amplification). The method was used to measure the $k_1/k_0$ ratio for the light-induced removal of HCl from 1,1-dichloro-ethylene. The agreement with the results obtained by other methods for the ratio of the rate constants was satisfactory[58].

The drawback of using a diffraction grating in the "equal amplification temperature" method is that only the ratios of constants for transitions with relatively high amplification can be measured, since the radiation losses in the resonator are rather high. This disadvantage can be overcome by combining the tandem laser configuration and the diffraction grating, as in the "zero amplification temperature" method[58].

### 2. The "Zero Amplification Temperature" Method

The method[58] relies on the fact that the relative amplification of the lines in the $P$ and $R$ branches has different dependences on $J$ and $T$. If $N_v/N_{v-1} < 1$, a single transition in the $P$ branch will have a positive amplification over a range of temperature, but on raising the temperature the amplification will change sign. On the other hand, if $N_v/N_{v-1} > 1$, the transition in the $R$ branch will have positive amplification at certain temperatures but the amplification will become negative as the temperature is lowered. At almost any ratio of the level occupancies (not too close to unity) there will be transitions in the $P$ and $R$ branches with zero amplification at accessible temperatures. The temperature at which the amplification of the transition changes from positive to negative has been termed the "zero amplification temperature".

The apparatus includes two laser tubes within a single resonator (tandem scheme). The resonator consists of a mirror and a diffraction grating in the Littrow configuration, which allows operation of the laser only on one (chosen) transition. The "leading" reaction in one tube should have enough amplification to emit radiation from this transition without assistance from the "subsidiary" reaction in the second tube, for which we wish to measure the ratio of the rate constants. If the "subsidiary" reaction gives positive amplification for the transition being studied, the time lag will be shorter than in the absence of the "subsidiary" reaction. Conversely, if the "subsidiary" reaction gives negative amplification the time lag increases. By varying the temperature of the "subsidiary" reaction we can determine the "zero amplification temperature" of this reaction. The occupancy ratio can then be found from the "zero amplification" equation, obtained by equating to zero the amplification expression [Eqn.(39)]:

$$\frac{N_v}{N_{v-1}} = \frac{B_{v-1}}{B_v}\exp\left\{\frac{hc}{kT_{za}}[B_vJ(J\mp1) - B_{v-1}J(J\pm1)]\right\}$$

where the upper sign refers to the transition $P_v \to v-1$. .$[(J-1) \to J]$ and the lower sign refers to the transition $R_v \to v-1[J \to (J-1)]$; $T_{za}$ is the zero amplification temperature.

The "zero amplification temperature" method usefully complements the "equal amplification temperature" method. Each has a number of advantages, depending on the properties of the reaction of interest. The "zero amplification temperature" method needs a suitable "leading" reaction, offering stable generation of the required transitions with an amplification sufficient to overcome the relatively large losses in the resonator. If such a reaction can be found, the results are more readily interpretable than those of the "equal amplification temperature" method. In particular, there is no need to correct for vibrational–rotational interaction or for the pressure dependence of the line shape.

### 3. Determination of the Temperature Dependence of the Ratio of Constants

Though the chemiluminescence and molecular beam methods give qualitative information on the effect of temperature on the reactions of interest, a quantitative interpretation is very difficult. Chemical lasers offer a far more satisfactory

method of studying the temperature dependence of the distribution of the reaction product over the vibrational states. In the laser experiments the temperature is the primary experimental variable, and the conditions are chosen so as to ensure precisely defined rotational and translational temperatures.

Both the "equal amplification temperature" and the "zero amplification temperature" method can be used to obtain temperature dependences. The former can be used because the transitions with maximum amplification vary with temperature. For example[59], in the F + $D_2$ removal reaction the "equal amplification temperature" for the $P_3(4)-P_3(5)$ transitions ($v = 3 \rightarrow 2$ band) of the product DF is 301 K, for the $P_3(5)-P_3(6)$ transitions it is 567 K, and for the $P_3(3)-P_3(4)$ transitions it lies below 153 K. This gives the temperature dependence of the $k_3/k_2$ ratio.

The "zero amplification temperature" method can be used to obtain temperature dependence because transitions with different $J$ values have different "zero amplification temperatures". Transitions for which the "zero amplification temperature" is accessible must be chosen. The method has been used[59] to determine the temperature dependence of the ratios of constants $k_v/k_{v-1}$ for the F + $H_2$ removal reaction. For the $v = 3 \rightarrow 2$ band the measurements were carried out on transitions of the $P$ branch, since in this case $k_3/k_2 < 1$. The "leading" reaction was F + HBr → $HF^+$ + Br. For the $v = 2 \rightarrow 1$ band the measurements were made on the $R$ branch because in this case $k_2/k_1 > 1$. This time the "leading" reaction was F + $CH_4$ → $HF^+$ + $CH_3$. By using a combination of the "equal amplification temperature" and the "zero amplification temperature" method the temperature dependence of the ratios of constants $k_3/k_2$ and $k_2/k_1$ was obtained[59]. The combined method has also been used[60] to study the effect of rotation on the distribution of vibrational energy in the F + $H_2$ reaction at different temperatures by using hydrogen enriched with the *para*-modification.

The temperature dependence of the ratio of constants has been obtained[61] also for another class of reactions: insertion–removal between NH and fluoromethanes. Though the flash photolysis of $HN_3$ in the presence of fluorinated methanes and argon does not yield laser generation, it was possible to measure the $k_v/k_{v-1}$ ratios as a function of temperature for $CF_4$, $CF_3H$, and $CF_2H_2$ by using the "zero amplification temperature" method in a tandem scheme.

## 4. The "Diffraction Grating Selection" Method

This method relies on a frequency-selective resonator consisting of a mirror and a diffraction grating in the Littrow configuration. As mentioned above this resonator allows the laser to be operated on a single, chosen, vibrational–rotational transition. Measurements of the relative time lags of the various transitions can be used to characterise the vibrational population inversion in terms of the optical amplification coefficients[15]. According to Patel[62],

$$\alpha_{v,J\rightarrow v',J'} = (\text{const})\, \nu \Delta\nu_D^{-1} |R_{v,J\rightarrow v',J'}|^2 \left(\frac{N_{v,J}}{g_J} - \frac{N_{v',J'}}{g_{J'}}\right) H^P_{v,J\rightarrow v',J'} \quad (41)$$

where $\nu$ is the frequency of the transition and $\Delta\nu_D$ is its Doppler width. Furthermore,

$$|R_{v,J\rightarrow v',J'}|^2 = |M_{v\rightarrow v'}|^2 S_{J'} F_{v,J\rightarrow v',J'}$$

where $M_{v \rightarrow v'}$ is a matrix element of the transition, $S_{J'} \equiv J'$ for transitions of the $P$ branch and $S_{J'} \equiv J' + 1$ for transitions of the $R$ branch, $F_{v,\ J\rightarrow v',\ J'}$ is the vibrational–rotational interaction factor, and $H^P_{v,\ J\rightarrow v',\ J'}$ is a correction factor for the line width, depending on the pressure, which includes the Doppler and the collision broadening. For a rotationally thermalised sample we have

$$N_{v,J} = N_v g_J \exp[-\Delta E^v_{\text{rot}}(J)/kT]/Q^v_{\text{rot}}$$

where $\Delta E^v_{\text{rot}}(J)$ is the rotational energy of the state ($v$, $J$), and $Q^v_{\text{rot}}$ is the rotational distribution function.

The amplification coefficients were calculated from published data on the transition frequencies, rotational energies, vibrational matrix elements, vibrational–rotational interaction factors, and collision line widths. For the amplification to be positive, the population inversion ($N_{v,\ J}/g_J - N_{v',\ J'}/g_{J'}$) in Eqn.(41) must be positive. This requirement leads to the following conditions: for a transition in the $R$ branch

$$\frac{N_v}{N_{v-1}} \geqslant \frac{Q^v_{\text{rot}}}{Q^{v-1}_{\text{rot}}} \exp\left(\frac{\Delta E^v_{\text{rot}}(J+1) - \Delta E^{v-1}_{\text{rot}}(J)}{kT}\right)$$

and for a transition in the $P$ branch

$$\frac{N_v}{N_{v-1}} \geqslant \frac{Q^v_{\text{rot}}}{Q^{v-1}_{\text{rot}}} \exp\left(\frac{\Delta E^v_{\text{rot}}(J-1) - \Delta E^{v-1}_{\text{rot}}(J)}{kT}\right),$$

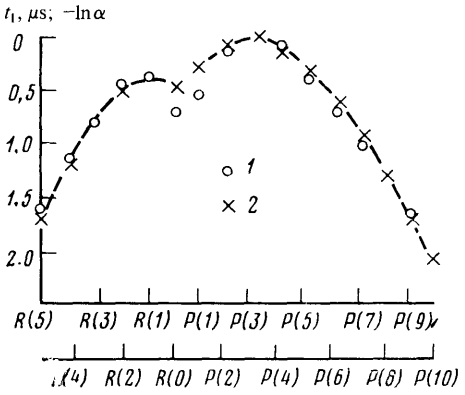



**Figure 4.** Comparison of the experimentally determined delay time $t_1$ (*1*) and the calculated values ln α (*2*) for $v = 2 \rightarrow 1$ transitions in HF. The amplification coefficients were calculated by Eqn.(41) for $N_2/N_1 = 3.35$ (without allowing for the factor $H^P_{v,\ J\rightarrow v',\ J'}$). The −ln α values for the $P_2(3)$ and $P_2(8)$ transitions were fitted to the measured delay times by using the expression $\alpha = \exp(-at_1)$. Introducing the pressure correction into Eqn.(41) improves the agreement for $N_2/N_1 = 3.45$ and the correspondence between the $R_2(0)$ and $P_2(1)$ transitions, which have anomalously high collision line widths.

Thus we can obtain the lower limits for $N_v/N_{v-1} = k_v/k_{v-1}$ by suitably choosing the experimental conditions (no relaxation effects, rotational equilibrium, constant temperature during the laser action). Furthermore these quantities can be determined by comparing experimentally measured time lags with calculations by the empirical equation $\alpha = \exp(-at_1)$, where $a$ is an empirical constant.

The agreement between experimental and calculated values of $t_1$ is optimised by varying $N_v/N_{v-1}$ in Eqn.(41). The procedure is illustrated in Fig.4 for the transitions of the

$v = 2 \rightarrow 1$ band of the HF molecule formed in the reaction $F + H_2$. In this way the $k_v/k_{v-1}$ ratios have been determined for the reactions $F + H_2$, $F + D_2$, F + HD, and F + DH.[15] The results are given in Table 4. For comparison the Table also gives some values of $k_v/k_{v-1}$ obtained by i.r. chemiluminescence and corrected (for the first time) for $(v, v)$ and $(v, R, T)$ energy transfer. The $v-v$ exchange for $HF \rightarrow HF$ and $HF \rightarrow H_2$ and the $v-R, T$ exchange with HF, $H_2$, F, Ar, $CF_3I$, and $N_2H_4$ have been calculated[63]. It was shown that for the $F + H_2$ reaction the initial $N_2/N_1$ ratios (equal to $k_2/k_1$) should be greater than those measured at time $t_1$. The ratio $N_3/N_2$ is almost insensitive to the energy exchange processes, whereas $N_1/N_0$ is extremely sensitive and very difficult to determine.

Table 4. $k_v/k_{v-1}$ ratio for the HF (DF) molecules formed by removal reactions at 300 K.

| Reaction | $k_4/k_3$ | $k_3/k_2$ | $k_2/k_1$ | $k_1/k_0$ | Ref. |
|---|---|---|---|---|---|
| $F+H_2 \rightarrow HF+H$ | — | 0.63±0.04 (0,62)* | 3,40±0.10 (3,8)* | 5.2±0.4 (>10)* | [15] |
| » | — | 0.48±0.01 (0,45)* | 3.3 | — | [59] |
| » | — | 0.58±0.12** | 3.6±0.2 ** | — | [5] |
| » | — | 0.53±0.1** | 3.4±0.7 ** | — | [12] |
| » | — | 0.56±0.06** | 3.4±0.3** | — | [64] |
| $F+D_2 \rightarrow DF+D$ | 0.4±0.2 ** | 1.80±0.10 | 2.35±0.10 | 2.3±0.2 | [15] |
| » | — | 1.6 | — | — | [51] |
| » | — | 1.5±0.1 | — | — | [59] |
| » | 0.66±0.13 ** | 1.5±0.3** | 2.3** | — | [12] |
| $F+HD \rightarrow HF+D$ | — | 0.15±0.05 *** | 3.1±0.2 | 5.2±0.4 | [15] |
| $F+DH \rightarrow DF+H$ | 0.3±0,2*** | 1.60±0.10 | 2.25±0.10 | 2.2±0.2 | [15] |

*Including energy exchange correction[63].

**Measured by i.r. chemiluminescence: all other values obtained by a chemical laser method.

***Estimated from the intensity of the laser bands in the free oscillation regime.

The "diffraction grating selection" method can be used to study some isotope effects[15]. Obviously,

$$\alpha_{v,J \rightarrow v'J'} = N_{\text{tot}}, \alpha'_{v,J \rightarrow v',J'}$$

where $N_{\text{tot}}$ is the total number of HF molecules and $\alpha'$ is the amplification coefficient per molecule.

If the reactant concentrations in the $F + H_2$ and F + HD systems are chosen so as to give identical amplification coefficients for the same transitions (as shown by the equality of the time lags) we can write

$$k_{F+H_2}[H_2]_0 \alpha'_{F+H_2} = k^{HF}_{F+HD}[HD]_0 \alpha'_{F+HD}$$

for equal concentrations of atomic fluorine in the two experiments and $[F] \ll [H_2]_0$, $[HD]_0$; $k^{HF}_{F+DF}$ is the rate constant of the reaction $F + HD \rightarrow HF^{\dagger} + D$. These experiments gave $k^{HF}_{F+HD}/k_{F+H_2} = 0.38 \pm 0.03$ at 300 K, and $k^{DF}_{F+HD}/k_{F+D_2} = 0.50 \pm 0.03$, where $k^{DF}_{F+DH}$ is the rate constant of the reaction $F + DH \rightarrow DF^{\dagger} + H$.

By combining these results with the kinetic isotope effect $k_{F+H_2}/k_{F+D_2} = 1.79 \pm 0.10$ at 300 K (obtained by measuring the full emission intensity in the free generation regime) we can calculate the intramolecular kinetic isotope effect $k^{HF}_{F+HD}/k^{DF}_{F+HD} = 1.4 \pm 0.1$ at 300 K.

The "grating selection" method has been used to study the distribution of vibrational energy in the HCl molecules formed by flash photolysis of different chloro-ethylenes[65]. Since vibrational relaxation was negligible under the conditions of those experiments we can write $N_v/N_{v-1} = k_v/k_{v-1}$. The results are shown in Table 5. For comparison the $k_v/k_{v-1}$ values obtained by the "equal amplification temperature method" in several forms are also shown in the Table.

Table 5. $k_v/k_{v-1}$ ratios for HCl molecules formed by photoremoval from M molecules at 300 K.

| M | $k_4/k_3$ | $k_3/k_2$ | $k_2/k_1$ | $k_1/k_0$ | Method |
|---|---|---|---|---|---|
| $CH_2=CHCl$ | 0.78±0.01 | 0.91±0.01 | 0.90±0.02 | 0.86±0.03 | I |
| $CH_2=CDCl$ | 0.86 | 1.05 | 0.91 | 0.81 | I |
| $CH_2=CCl_2$ | 0.83±0.02 | 1.02±0.03 | 0.97±0.01 | 0.75±0.03 | I |
| $CH_2=CCl_2$ | — | 0.87±0.02 | — | — | II |
| $CH_2=CCl_2$ | — | — | 1.08±0.03 | — | III |
| $CH_2=CCl_2$ | — | 1.06 | 1.07 | 0.78 | IV |
| *Cis*-CHCl=CHCl | — | 0.72 | 0.83 | 0.79 | I |
| | — | — | 0.81±0.02 | — | II |
| | — | 0.71±0.03 | 0.76±0.02 | — | III |
| *Trans*-CHCl=CHCl | — | 0.62 | 0.65 | 0.69 | I |
| | — | — | 0.70±0.02 | — | II |
| $CHCl=CCl_2$ | — | 0.72 | 0.74 | 0.69 | I |

Notes. Methods: I) diffraction grating selection[65], II) equal amplification temperature[56], III) and IV) equal amplification temperature with a tandem arrangement[57] or a diffraction grating[58].

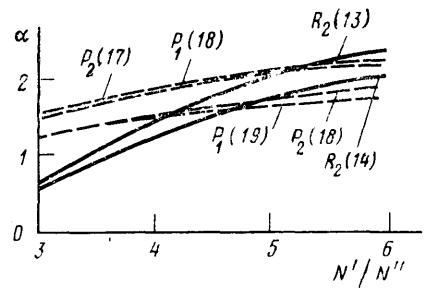



**Figure 5.** Relative amplification coefficients α as a function of the population inversion $N'/N''$ for some rotational transitions of the $A \rightarrow X$ (0, 0) band of the CN radical, calculated by assuming rotational and spin-orbit equilibrium of the CN* radical ($A^2\Pi_i$ at 300 K).

The frequency-selective resonator has been used also[66] to determine the ratio of the populations of the upper and the lower level of a laser working on an electronic transition of the CN radical formed by flash photolysis of methyl isocyanide. The relative optical amplification coefficients for the laser transitions in this case were calculated from the expression

$$\alpha = \text{const} \cdot S_{J'} \left( \frac{N'}{N''} \frac{\exp(-E'_{\text{rot}}/kT)}{Q'_{\text{rot}}} - \frac{\exp(-E''_{\text{rot}}/kT)}{Q''_{\text{rot}}} \right) \left( \frac{N'}{N''} + 1 \right)^{-1} \quad (42)$$

where $S_{J'}$ is the intensity of the rotational line, and the primes ' and " refer respectively to the upper ($A^2\Pi_i$, $v' = 0$)

and the lower ($X^2\Sigma^+$, $v''=0$) laser level. The relative amplification coefficients are shown in Fig.5 as a function of the population inversion for several transitions of the $A \rightarrow X$ (0, 0) band of the CN radical. The intersections of these lines give the lower limits of the ratio $N'/N''$. For example, the transition $R_2$ (13) begins to emit before the transition $P_1$ (18), and therefore it has a greater amplification. This gives $N'/N'' > 5.1$. By comparing the curves for different transitions we see that $N'/N'' \cong k'/k'' > 5.3$, where $k'$ and $k''$ are the rate constants of the processes which populate the upper and the lower level respectively. Similar calculations of the population ratio of the upper and the lower level can be made without a selective resonator for a laser working in the free generation regime, but in this case Eqn.(42) is applied only to the transition with maximum amplification. In this way the ratios $N'/N'' \cong k'/k''$ have been obtained for the populations of the upper ($A^2\Pi_{3/2}$, $v'=0$) and the lower ($X^2\Sigma^+$, $v''=0$) level of the CN radical formed by flash photolysis of $CH_3NC$, $CF_3CN$, HCN, $C_2F_5CN$, $(CN)_2$, and BrCN.[67]

The method has been used also to determine the population ratio of the upper and the lower level in HF and HCl molecules formed by insertion–removal reactions between $O(^1D)$ and fluorinated and chlorinated methanes[68–70]. The results are shown in Table 6.

Table 6. Estimates of the population ratios $N_v/N_{v-1} = k_v/k_{v-1}$ from the maximum amplification transitions for $O(^1D)$ + M addition–removal reactions.

| M | Emitting molecule | $v$ | $k_v/k_{v-1}$ |
|---|---|---|---|
| $CHF_3$ | HF | 2 | 0.8 [68] |
| $CH_3F$ | HF | 1 | 0.35 [68] |
| $CHCl_3$ | HCl | 1 | 0.50 [69] |
| $CH_3Cl$ | HCl | 1 | 0.61 [69] |
| $CHCl_2F$ | HF | 2 | 0.8 [70] |
| $CHCl_2F$ | HCl | 1 | 0.5 [70] |
| $CHClF_2$ | HF | 2 | 0.8 [70] |

The "grating selection" method was applied[71] in the determination of the relative population of levels in the HF molecule formed by the insertion–removal reaction $O(^3P)$ + fluoro-ethanes. The result was $N_1/N_0 \cong k_1/k_0 = 0.52 \pm 0.02$ for $C_2H_3F$ and $N_1/N_0 \cong k_1/k_0 = 0.61 \pm 0.04$ for *cis* and *trans*-1,2-$C_2H_2F_2$ and $C_2HF_3$.

Thus the laser generation produced by chemical reactions in a resonator can yield important information on the rate of elementary processes in the reaction medium. Laser methods can be used to measure the rate constants of the reactions of atoms and radicals with molecules, the rates of transfer and relaxation of vibrational excitation, and the rate constants for the formation of the reaction product in different energy states. The use of competing reactions widens the scope of the laser methods and allows the rate constants of processes which are not true "laser" reactions to be determined. Thus the method has adequate generality. In spite of the many assumptions made in the oscillation delay time and oscillation decay methods, rate constants can be determined to a precision comparable to that of other methods. However, no other method is comparable to the laser methods for determining the state of vibrationally excited products.

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